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13. ABSTRACT (Maximum 200 words) Reactions between AlX_3 ($X = Cl, Br$) and $P(SiMe_3)_3$ afforded the adducts $X_3Al \cdot P(SiMe_3)_3$. $Et_2AlP(SiMe_3)_2Al(Et)_2As(SiMe_3)_2$ was obtained from the equilibration of $[Et_2AlP(SiMe_3)_2]_2$ and $[Et_2AlAs(SiMe_3)_2]_2$. Reactions of Me_3Al with Ph_2AsH and $Ph(Me_3SiCH_2)AsH$ afforded $[Me_2AlAsPh_2]_3 \cdot (C_7H_8)_2$ and $[Me_2AlAs(CH_2SiMe_3)Ph]_3$. Reactions of Ph_3Al with $E(SiMe_3)_3$ ($E = P$ or As) afforded $Ph_3Al \cdot E(SiMe_3)_3$ [$E = P, As$, respectively], and Ph_2AlCl with $E(SiMe_3)_3$ ($E = P, As$) yielded $Ph_2(Cl)Al \cdot E(SiMe_3)_3$ [$E = P, As$]. $Ph(Cl)_2Al \cdot P(SiMe_3)_3$ was obtained from $PhAlCl_2$ and $P(SiMe_3)_3$, and reactions of Et_3Ga and $(Me_3SiCH_2)_3In$ with $Sb(SiMe_3)_3$ yielded $Et_3Ga \cdot Sb(SiMe_3)_3$ and $(Me_3SiCH_2)_3In \cdot Sb(SiMe_3)_3$, respectively. Reaction of $(Me_3CCH_2)_2GaCl$ or $(Me_3SiCH_2)_2InCl$ with $Sb(SiMe_3)_3$ afforded $[(Me_3CCH_2)_2GaSb(SiMe_3)_2]_x$ and $[(Me_3SiCH_2)_2InSb(SiMe_3)_2]_2$, respectively. Reaction of $GaCl_3$ with $Sb(SiMe_3)_3$ affords an intermediate material which, upon thermolysis, yields nanocrystalline $GaSb$ with an approximate average particle size of 12 nm. Reaction of $(Me_3SiCH_2)_3Al$ with $E(SiMe_3)_3$ ($E = P, As$) gave $(Me_3SiCH_2)_3AlP(SiMe_3)_3$ and $(Me_3SiCH_2)_3AlAs(SiMe_3)_3$, and reaction of $(Me_3CCH_2)_3Al$ with $E(SiMe_3)_3$ ($E = P, As$) gave $(Me_3CCH_2)_3AlP(Me_3SiCH_2)_3$ and $(Me_3CCH_2)_3AlAs(SiMe_3)_3$. $(Me_3SiCH_2)_2(Br)AlP(Me_3SiCH_2)_3$ was obtained from the reaction of $(Me_3SiCH_2)_2AlBr$ with $P(SiMe_3)_3$. $[Me_3SiCH_2(Br)AlP(SiMe_3)_2]_2$ and $[Me_3SiCH_2(Br)AlAs(SiMe_3)_2]_2$ were isolated as rearrangement products of the 1:1 lithium halide elimination reactions of $(Me_3SiCH_2)_3AlBr$ with $Li(SiMe_3)_2$ ($E = P, As$). This metathetical system also led to the isolation of $[(Me_3SiCH_2)_2AlP(SiMe_3)_2]$ and $[(Me_3SiCH_2)_2AlAs(SiMe_3)_2]_2$.				
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Dr. Harold E. Guard

Final Report

**SYNTHESIS AND STUDIES OF
ALUMINUM-NITROGEN, -PHOSPHORUS AND ARSENIC
CYCLES AND CLUSTERS**

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**Final Report for AASERT Grant #N00014-93-1-0860 R&T Project 4135008---13
01 June 1993 through 30 September 1996**

**SYNTHESIS AND STUDIES OF
ALUMINUM-NITROGEN, -PHOSPHORUS AND ARSENIC
CYCLES AND CLUSTERS**

1.0 Summary

The attempted dehalosilylation reactions between AlX_3 ($\text{X} = \text{Cl}, \text{Br}$) and $\text{P}(\text{SiMe}_3)_3$ in toluene in 1:1 mole ratios afforded only the adducts $\text{Cl}_3\text{Al}\cdot\text{P}(\text{SiMe}_3)_3$ (**1**) and $\text{Br}_3\text{Al}\cdot\text{P}(\text{SiMe}_3)_3$ (**2**), respectively. Compounds **1** and **2** were characterized by ^1H , ^{13}C , ^{27}Al , and ^{31}P solution NMR spectroscopy, as well as partial elemental analysis. In addition, the solid state structures of the toluene solvates of **1** and **2** were determined by single-crystal X-ray analysis. Characterization revealed that the solid solvated adducts **1** and **2** are isostructural and their crystals are isomorphous. In each compound, the Al and the P atoms reside in tetrahedral environments, with each $\text{X}_3\text{Al}\cdot\text{P}(\text{SiMe}_3)_3$ ($\text{X} = \text{Cl}, \text{Br}$) molecule associated with one interstitial toluene molecule in the crystals. These adducts are noteworthy in that they possess extremely short, essentially equal Al-P bond lengths [For **1**: $\text{Al}-\text{P} = 2.392(4) \text{ \AA}$, and for **2**: $\text{Al}-\text{P} = 2.391(6) \text{ \AA}$], which are the shortest found to date in aluminum-phosphorus molecular species.

The aluminum mixed-pnicogen compound $\text{Et}_2\text{AlP}(\text{SiMe}_3)_2\text{Al}(\text{Et})_2\text{As}(\text{SiMe}_3)_2$ (**3**) is the first structurally-characterized compound to contain a four membered ring with two aluminum centers bridged by two different heavier group 15 atoms. Compound **3** was synthesized by the equilibration of $[\text{Et}_2\text{AlP}(\text{SiMe}_3)_2]_2$ (**4**) and $[\text{Et}_2\text{AlAs}(\text{SiMe}_3)_2]_2$ (**5**) in a 1:1 mole ratio under ultrasonic conditions. Low-temperature X-ray crystallographic analysis revealed that crystals of **3** belong to the monoclinic system, space group $C2/c$ (C_{2h}^6), with unit cell dimensions of $a = 17.960(4)$, $b = 9.328(1)$, $c = 20.194(5) \text{ \AA}$, and $\beta = 100.33(2)^\circ$ for $Z = 4$, and isomorphous with those of **4** and **5**. The electron ionization (20 eV) mass spectrum of **3** shows a fragmentation pattern consistent with this compound and no peaks above m/z 400 consistent with either **4** or **5**.

The reactions of trimethylaluminum with diphenylarsine, Ph_2AsH , and phenyl(trimethylsilylmethyl)arsine, $\text{Ph}(\text{Me}_3\text{SiCH}_2)\text{AsH}$, in 1:1 mole ratios afford the trimeric compounds $[\text{Me}_2\text{AlAsPh}_2]_3\cdot(\text{C}_7\text{H}_8)_2$ (**6**) and $[\text{Me}_2\text{AlAs}(\text{CH}_2\text{SiMe}_3)\text{Ph}]_3$ (**7**), respectively. Compounds **6** and **7** are the first Al-As six-membered ring compounds to be structurally characterized by single-crystal X-ray crystallography, as well as ^1H and ^{13}C solution NMR spectroscopy. X-ray crystallographic analysis revealed that trimer **6** is a toluate which crystallizes in the monoclinic space group $P 2_1/n$, with $a = 14.549(6) \text{ \AA}$, $b = 22.838(7) \text{ \AA}$, $c = 16.891(4) \text{ \AA}$, and $\beta = 105.12(5)^\circ$ for $Z = 4$. Trimer **7** crystallizes in the triclinic system, space group $P\bar{1}$, and has two unique molecules in a unit cell with dimensions of $a = 15.619(7) \text{ \AA}$, $b = 17.487(6) \text{ \AA}$, $c = 19.863(6) \text{ \AA}$, $\alpha = 94.86(3)^\circ$, $\beta = 101.41(3)^\circ$, and $\gamma = 113.34(3)^\circ$ for $Z = 4$. The six-membered Al-As rings in both **6** and **7** occupy chair conformations, furnishing both trimers with structural characteristics similar to cyclohexane. The Al and As centers of both **6** and **7** reside in pseudotetrahedral environments, with the Al-As bond lengths ranging from $2.512(3) \text{ \AA}$ to $2.542(3) \text{ \AA}$ in **6**, and from $2.504(5) \text{ \AA}$ to $2.526(5) \text{ \AA}$ in **7**.

The independent reactions of Ph_3Al with $\text{E}(\text{SiMe}_3)_3$ ($\text{E} = \text{P}$ or As) in 1:1 mole ratios afforded the adducts $\text{Ph}_3\text{Al}\cdot\text{E}(\text{SiMe}_3)_3$ [$\text{E} = \text{P}$ (**8**) and As (**9**), respectively]. The attempted dehalosilylation reactions between Ph_2AlCl and $\text{E}(\text{SiMe}_3)_3$ ($\text{E} = \text{P}$ or As) in 1:1 mole ratios yielded only the adducts $\text{Ph}_2(\text{Cl})\text{Al}\cdot\text{E}(\text{SiMe}_3)_3$ [$\text{E} = \text{P}$ (**10**) and As (**11**)]. The adduct $\text{Ph}(\text{Cl})_2\text{Al}\cdot\text{P}(\text{SiMe}_3)_3$ (**12**)

was isolated from the reaction of equimolar amounts of PhAlCl_2 and $\text{P}(\text{SiMe}_3)_3$. Compounds **8-12** were characterized by NMR spectroscopy and partial elemental analysis. In addition, the solid-state structures of **8-10** were determined by single-crystal X-ray analysis. Compound **8** crystallizes in the monoclinic space group $P 2_1/n$ (C_{2h}^5), while **9** crystallizes in the triclinic space group $P -1(C_1^1)$, each with two discrete molecules per asymmetric unit. Crystals of compound **10** belong to the orthorhombic space group $P 2_12_12_1(D_2^4)$. Compounds **8-10** are the first structurally-characterized compounds to contain phenyl-substituted Al centres bonded to heavier pnictogen atoms.

The independent 1:1 reactions of Et_3Ga and $(\text{Me}_3\text{SiCH}_2)_3\text{In}$ with $\text{Sb}(\text{SiMe}_3)_3$ yield the simple Lewis acid-base adducts $\text{Et}_3\text{Ga} \cdot \text{Sb}(\text{SiMe}_3)_3$ (**13**) and $(\text{Me}_3\text{SiCH}_2)_3\text{In} \cdot \text{Sb}(\text{SiMe}_3)_3$ (**14**), respectively. Reaction of $(\text{Me}_3\text{CCH}_2)_2\text{GaCl}$ or $(\text{Me}_3\text{SiCH}_2)_2\text{InCl}$ with $\text{Sb}(\text{SiMe}_3)_3$ in a 1:1 mole ratio affords the dehalosilylation products $[(\text{Me}_3\text{CCH}_2)_2\text{GaSb}(\text{SiMe}_3)_2]_x$ (**15**) and $[(\text{Me}_3\text{SiCH}_2)_2\text{InSb}(\text{SiMe}_3)_2]_2$ (**16**), respectively. These new compounds were characterized by multinuclear solution NMR (^1H and ^{13}C), partial elemental analysis and for **13**, **14**, and **16**, single crystal X-ray analysis.

The 1:1 reaction of GaCl_3 with $\text{Sb}(\text{SiMe}_3)_3$ in pentane solution affords an intermediate material which, upon thermolysis, yields nanocrystalline GaSb (**17**) with an approximate average particle size of 12 nm. The product was characterized through powder X-ray diffraction, elemental analysis, and HRTEM.

Reaction of $(\text{Me}_3\text{SiCH}_2)_3\text{Al}$ with $\text{E}(\text{SiMe}_3)_3$ ($\text{E} = \text{P}, \text{As}$) in a 1:1 mole ratio affords the Lewis acid-base adducts $(\text{Me}_3\text{SiCH}_2)_3\text{AlP}(\text{SiMe}_3)_3$ (**18**) and $(\text{Me}_3\text{SiCH}_2)_3\text{AlAs}(\text{SiMe}_3)_3$ (**19**). Similarly, the 1:1 mole ratio reaction of Np_3Al with $\text{E}(\text{SiMe}_3)_3$ ($\text{E} = \text{P}, \text{As}$) leads to the isolation of $(\text{Me}_3\text{CCH}_2)_3\text{AlP}(\text{SiMe}_3)_3$ (**20**) and $(\text{Me}_3\text{CCH}_2)_3\text{AlAsT}(\text{SiMe}_3)_3$ (**21**). The adduct $(\text{Me}_3\text{SiCH}_2)_2(\text{Br})\text{AlP}(\text{SiMe}_3)_3$ (**22**) was obtained from the 1:1 mole ratio reaction of $(\text{Me}_3\text{SiCH}_2)_2\text{AlBr}$ with $\text{P}(\text{SiMe}_3)_3$. The dimers $[\text{Me}_3\text{SiCH}_2(\text{Br})\text{AlP}(\text{SiMe}_3)_2]_2$ (**23**) and $[\text{Me}_3\text{SiCH}_2(\text{Br})\text{AlAs}(\text{SiMe}_3)_2]_2$ (**24**) were isolated as rearrangement products of the 1:1 lithium halide elimination reactions of $(\text{Me}_3\text{SiCH}_2)_2\text{AlBr}$ with $\text{LiE}(\text{SiMe}_3)_2$ ($\text{E} = \text{P}, \text{As}$). This metathetical system also led to the isolation of $[(\text{Me}_3\text{SiCH}_2)_2\text{AlP}(\text{SiMe}_3)_2]_2$ (**25**) and $[(\text{Me}_3\text{SiCH}_2)_2\text{AlAs}(\text{SiMe}_3)_2]_2$ (**26**). Various physical and spectroscopic data, including a multinuclear variable temperature NMR study of **23** and **24**, were obtained for the above compounds, along with the X-ray crystal structures of **19-24** and **26**.

2.0 Publications and Presentations at Meetings Describing Results Obtained

2.1 Publications

1. R. L. Wells, A. T. McPhail, J. A. Laske, and P. S. White, "Synthesis and Characterization of Aluminum-Phosphorus Adducts: X-ray Crystal Structures of $\text{Cl}_3\text{Al} \cdot \text{P}(\text{SiMe}_3)_3 \cdot \text{C}_7\text{H}_8$ and $\text{Br}_3\text{Al} \cdot \text{P}(\text{SiMe}_3)_3 \cdot \text{C}_7\text{H}_8$ ", *Polyhedron* **1994**, *13*, 2737.
2. J. A. Laske Cooke, R. L. Wells, and P. S. White, "First Example of an Aluminum-Phosphorus-Arsenic Mixed-Pnictogen Ring Compound: X-ray Crystal Structure of $\text{Et}_2\text{AlP}(\text{SiMe}_3)_2\text{Al}(\text{Et})_2\text{As}(\text{SiMe}_3)_2$ ", *Organometallics* **1995**, *14*, 3562.
3. J. A. Laske Cooke, A. P. Purdy, R. L. Wells, and P. S. White, "Reactions of Trimethylaluminum with Secondary Arsines: Synthesis and Characterization of Phenyl[(trimethylsilyl)methyl]arsine and the X-ray Crystal Structures of the Trimers $[\text{Me}_2\text{AlAsPh}_2]_3 \cdot (\text{C}_7\text{H}_8)_2$ and $[\text{Me}_2\text{AlAs}(\text{CH}_2\text{SiMe}_3)\text{Ph}]_3$ " *Organometallics* **1996**, *15*, 84.

4. J. A. Laske Cooke, H. Rahbarnoohi, A. T. McPhail, R. L. Wells, and P. S. White, "Reactions of Phenylaluminum Compounds with $E(\text{SiMe}_3)_3$ ($E = \text{P}$ or As): X-ray Crystal Structures of $\text{Ph}_3\text{Al}\cdot E(\text{SiMe}_3)_3$ ($E = \text{P}$ or As) and $\text{Ph}_2(\text{Cl})\text{Al}\cdot\text{P}(\text{SiMe}_3)_3$ ", *Polyhedron* **1996**, *15*, 3033.
5. R. A. Baldwin, E. E. Foos, R. L. Wells, P. S. White, A. L. Rheingold, and G. P. A. Yap, "Synthesis and Characterization of Potential Single-Source Precursors to Group 13-Antimonides", *Organometallics* **in press**.
6. R. A. Baldwin, E. E. Foos, and R. L. Wells, "Facile Preparation of Nanocrystalline Gallium Antimonide", *Mater. Res. Bulletin* **in press**.
7. R. L. Wells, E. E. Foos, A. L. Rheingold, L. M. Liable-Sands, P. S. White "Synthesis and Characterization of Alkylaluminum-Phosphorus and-Arsenic Compounds Incorporating the (Trimethylsilyl)methyl and neo-Pentyl Ligands", **in preparation**.

3.0 Presentations at Meetings

1. J. L. Laske, R. L. Wells, A. T. McPhail, and P. White, "Synthesis, Characterization and Decomposition Studies of Aluminum-Phosphorus Adducts: X-ray Crystal Structures of $\text{Me}_2(\text{Cl})\text{Al}\cdot\text{P}(\text{SiMe}_3)_3$ and $\text{X}_3\text{Al}\cdot\text{P}(\text{SiMe}_3)_3\cdot\text{C}_7\text{H}_8$ ($\text{X} = \text{Cl}, \text{Br}$)", Abstracts of Papers, 207th American Chemical Society National Meeting **1994**, INOR 479, San Diego, CA (paper presented by J. L. Laske, graduate student).
2. J. L. Laske, R. L. Wells, A. T. McPhail, and P. White, "Synthesis, Characterization and Decomposition Studies of Aluminum-Phosphorus Adducts: X-ray Crystal Structures of $\text{Me}_2(\text{Cl})\text{Al}\cdot\text{P}(\text{SiMe}_3)_3$ and $\text{X}_3\text{Al}\cdot\text{P}(\text{SiMe}_3)_3\cdot\text{C}_7\text{H}_8$ ($\text{X} = \text{Cl}, \text{Br}$)", 108th Sectional Conference of the North Carolina Section of the American Chemical Society **1994**, Durham, NC (paper presented by J. L. Laske, graduate student).
3. R. A. Baldwin, S. R. Aubuchon, M. S. Lube, J. A. Laske, R. L. Wells, and P. S. White, "On the Preparation and Characterization of Binary and Ternary 13-15 Materials", Abstracts of Papers, 208th American Chemical Society National Meeting **1994**, INOR 406, Washington, DC (poster presented by R. A. Baldwin, graduate student).
4. M. S. Lube, R. L. Wells, L. J. Jones III, R. A. Baldwin, J. A. Laske, A. T. McPhail, and P. S. White, "Synthesis and Characterization of Potential Precursors to Ternary 13-15 Semiconductors", Abstracts of Papers, 208th American Chemical Society National Meeting **1994**, INOR 407, Washington, DC (poster presented by M. S. Lube, graduate student).
5. J. A. Laske, R. L. Wells, and P. S. White, "Organoaluminum-pnicogen Chemistry: Synthesis, Characterization and Decomposition Studies of Potential Precursors to AIP, AlAs, and $\text{Al}_x\text{Ga}_{1-x}\text{E}_y$ ($E = \text{P}, \text{As}$)", Abstracts of Papers, 209th American Chemical Society National Meeting **1995**, INOR 28, Anaheim, CA (paper presented by J. A. Laske, graduate student).
6. J. A. Laske, R. L. Wells, and P. S. White, "Organoaluminum-pnicogen Chemistry: Synthesis, Characterization and Decomposition Studies of Potential Precursors to AIP, AlAs, and $\text{Al}_x\text{Ga}_{1-x}\text{E}_y$ ($E = \text{P}, \text{As}$)", 109th Sectional Conference of the North Carolina Section of the American Chemical Society **1995**, Chapel Hill, NC (paper presented by J. A. Laske, graduate student).

7. J. A. Laske, H. Rahbarnoohi, R. L. Wells, A. T. McPhail, and P. S. White, "Reactions of Triphenylaluminum and Phenylaluminum halides with Silyl Pnicogen Compounds", Abstracts of Papers, 210th American Chemical Society National Meeting **1995**, INOR 28, Chicago, IL (paper presented by R. L. Wells).
8. R. A. Baldwin, E. E. Foos, R. L. Wells, G. P. A. Yap, and A. L. Rheingold, "Preparation and Characterization of Compounds Containing a Group 13 Element-Antimony Bond: Facile Synthesis of Nanocrystalline GaSb", Abstracts of Papers, 211th American Chemical Society National Meeting, March 24-29, **1996**, INOR 198, New Orleans, LA (poster presented by R. A. Baldwin and E. E. Foos, graduate students).
9. R. A. Baldwin, E. E. Foos, R. L. Wells, G. P. A. Yap, and A. L. Rheingold, "Preparation and Characterization of Compounds Containing a Group 13 Element-Antimony Bond: Facile Synthesis of Nanocrystalline GaSb", 110th Sectional Conference of the North Carolina Section of the American Chemical Society, Raleigh, NC, April 13, **1996**. (paper presented by E. E. Foos, graduate student).

2.2 Students Supported by the Grant

1. Janeen. A. Laske Cooke, June 1993 - September 1995; completed requirements for the Ph.D degree in September 1993.
2. Edward E.Foos, September 1995 - September 1996; currently a third-year graduate student.